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Hydrogen assisted catalytic biomass pyrolysis for green fuels. Effect of catalyst in the fluid bed.

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Fast pyrolysis of biomass is a well-known technology for producing bio-oil. However, in order to use the oil as transportation fuel the oxygen content must be decreased from approximately 40 wt.% to below 1 wt.%. This can be achieved by catalytic hydrodeoxygenation (HDO). Unfortunately, deactivation due to coking of the catalyst is an inhibitive problem for this technology. The objective of the present work is to produce oxygen free gasoline and diesel from biomass by hydrogen assisted catalytic fast pyrolysis. Fast pyrolysis of beech wood (feeding rate: 275 g/h) has been performed in 26 bar hydrogen (flow: 55-90 NL/min) in a fluid bed reactor operated at 450 °C with several different catalysts as bed material followed by an additional vapor phase, fixed bed HDO reactor (operated at 370-400 °C) using a commercial NiMoS/Al₂O₃ catalyst. The time on stream varied between 0.75 and 3.5 h. The tested catalysts in the fluid bed include olivine sand (OS), MgAl₂O₄ (MgAl), CoMo/MgAl₂O₄ (CoMo), zeolite mixed with alumina (ZA), NiMo impregnated on zeolite mixed with alumina (NiMoZA), and a cheap and non-toxic catalyst (HYCP).

The HYCP catalyst was tested both in reduced (HYCP-R) and sulfide forms (HYCP-S), while the other catalysts, with exception of OS, were sulfided prior to the experiment. Using both reactors, essentially oxygen free oil has been obtained with condensed oil and C₄₊ yields between 16 and 25 wt. % daf depending of the catalyst in the fluid bed (Figure 1), which corresponds to an energy recovery up to 58 %. Using MgAl and ZA gave a high char yield and a low yield of condensable organics compared to the supported active catalysts (CoMo and NiMoZA). Characterization of the spent catalyst with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) showed a significant higher carbon content on the spent support materials (MgAl and ZA) compared to the supported catalysts (CoMo and NiMoZA) and the HYCP catalysts. Using the HYCP-R in the fluid bed reactor and bypassing the HDO reactor decreased the C₁₋₃ yield from 12 to 3 wt. % daf and increased the condensable organic yield from 25 to 34 wt. % daf. However, the oxygen concentration in the produced oil increased to 14 wt. % db. GC×GC-MS/FID showed that the oxygenates were mainly phenols (22 % FID-area) and oxygenated aliphatics (21 % FID area). Our work indicates that hydrogen assisted catalytic pyrolysis is a feasible path for production of liquid renewable fuels. The catalyst in the fluid bed is essential and has a significant impact on the product distribution. It is possible to obtain a high yield of condensable organics with the HYCP catalyst, thus showing that it is not necessary to use expensive formulated catalysts. In our ongoing research the differences between CoMo, NiMo, Mo catalysts in the fluid bed is further investigated. Furthermore, the effect of the metal loading and the effect of using different supports are also studied and the spent catalysts characterized by use of SEM and transmission electron microscopy (TEM).

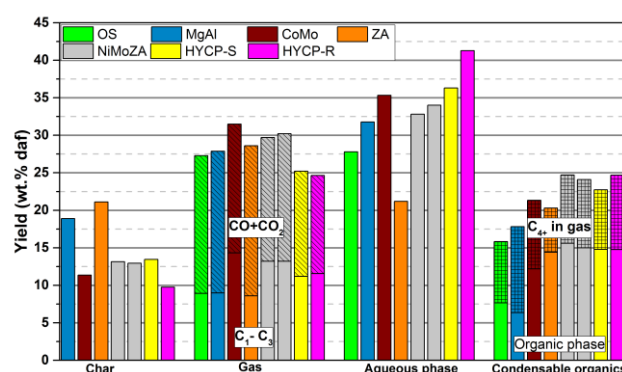


Figure 1. Effect of the catalyst in the fluid bed on the product distribution.